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Identification Of Carbonyls In Cigar Smoke by Hydrazone Exchange Gas Chromatography

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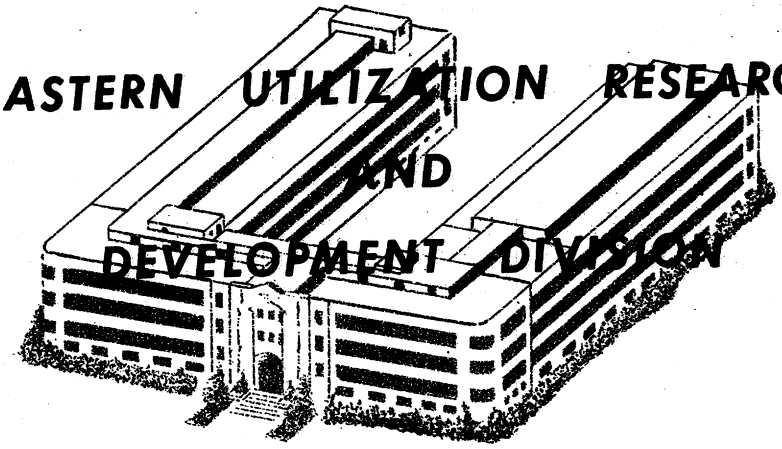
ABSTRACT

Several simple carbonyls have been detected in cigar smoke by means of a method utilizing hydrazone exchange and gas chromatography. These were formaldehyde, acetaldehyde, propanal, n-butanal and methyl ethyl ketone. Confirmation of the presence of acetone was obtained.

This is a report of work done at the

EASTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION



Philadelphia 18, Pa.

IDENTIFICATION OF CARBONYLS IN CIGAR SMOKE BY HYDRAZONE EXCHANGE GAS CHROMATOGRAPHY

by

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In connection with a study of the carbonyl components of cigar smoke, it was convenient to concentrate and separate these materials as their 2, 4-dinitrophenylhydrazones (DNPH's). In many cases this method yielded very small amounts of mixed derivatives. The identification of several components in these mixtures was accomplished by use of the recently developed method of Ralls for hydrazone exchange gas chromatography.[1]

The procedure employed was identical with that recommended by Ralls except for the chromatographic conditions. The gas chromatographic unit was a commercial model modified to provide adequate temperature control (± 0.3° C.). The detector was a four-filament thermal conductivity cell. The recorder had a sensitivity of 2.5 mv., a 3-second pen speed and a 30 in./hr. chart speed. Two columns were used: a 10-foot Carbowax 20M and a 5-foot Craig Polyester** (polymeric 1, 4-butanediol succinate), both coated

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**Mention of a specific commercial product in this paper does not necessarily constitute endorsement by the United States Department of Agriculture.

[1]Ralls, J. W., Rapid Method for Semiquantitative Determination of Aldehydes, Ketones and Acids. Analyt. Chem. 32: 332-333 (1960).

on Chromosorb (35/80 mesh) at 30 parts to 70 parts of Chromosorb, and packed in 1/4-inch stainless steel tubing. These were operated at 90° and 100° C., respectively, and at a helium flow rate of 32 ml./min. The usual detector cell current was 300 ma.

A series of known DNPH's were run, both singly and in pertinent synthetic mixtures, and their respective retention times measured. These are given in Table 1. The separation of a typical synthetic mixture is illustrated in Figure 1. The starting point is the time that the oil bath is

Table 1. Retention Times of Authentic Carbonyls

Compound	Retention Times (min.)*	
	Carbowax Column	Polyester Column
1. Formaldehyde	2.3	---
2. Acetaldehyde	3.1	1.2
3. Propanal	4.7	1.5
4. Acetone	5.2	1.3
5. iso-Butanal	5.3	1.3
6. 2, 2-Dimethyl Propanal	5.3	---
7. n-Butanal	7.1	1.8
8. Methyl Ethyl Ketone	8.1	2.0
9. 2-Methyl Butanal	8.9	2.0
10. iso Pentanal	9.0	2.1
11. Methyl iso-Propyl Ketone	9.7	2.0
12. 3, 3-Dimethyl Butanal	10.7	2.4
13. Diethyl Ketone	12.2	2.6
14. n-Pentanal	12.2	2.3
15. Methyl n-Propyl Ketone	12.3	2.3
16. Di-iso-Propyl Ketone	14.1	2.6
17. 2-Ethyl Butanal	14.4	2.7
18. Methyl iso-Butyl Ketone	14.5	2.7
19. Hexanal	21.6	3.8
20. Methyl n-Butyl Ketone	21.7	3.6
21. Di-n-Propyl Ketone	----	4.4
22. Heptanal	----	5.8
23. Methyl n-Amyl Ketone	38.5	6.3
24. 2-Hexenal	----	7.2
25. Methyl n-Hexyl Ketone	Not regenerated	
26. Diacetyl	Not regenerated	

* See text for conditions.

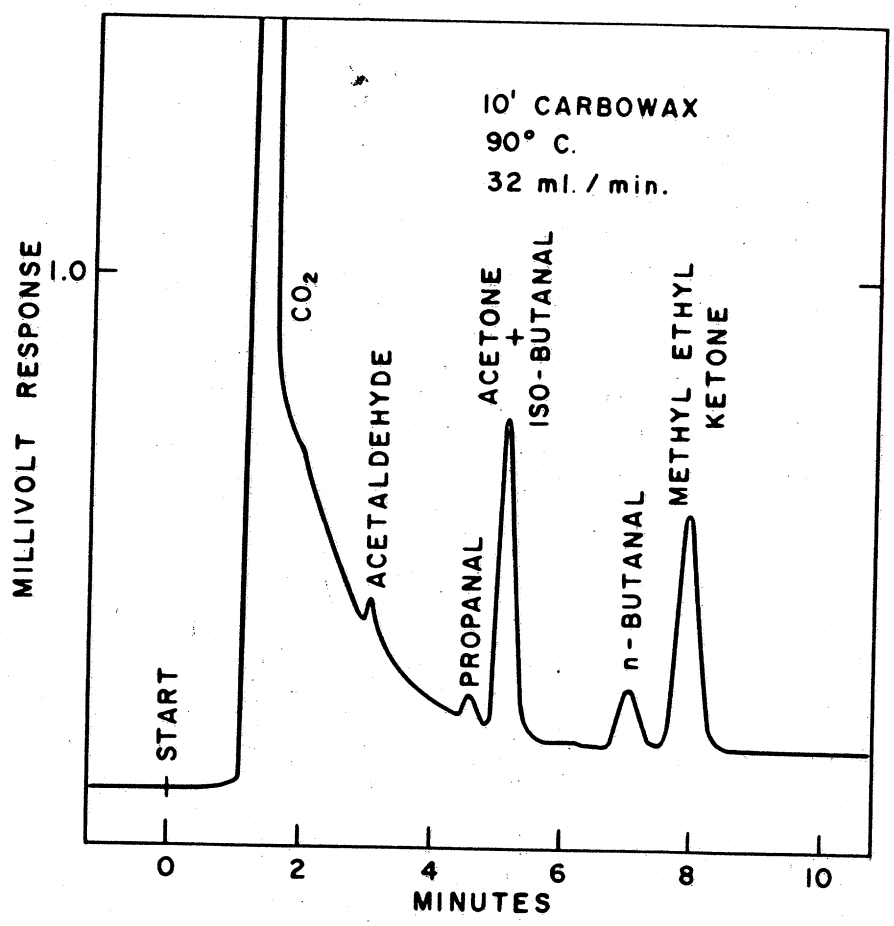

Figure 1. Separation of a synthetic mixture.

first brought into contact with the sample capillary to initiate the exchange reaction.[1] There is no air peak, because the system is completely swept out with helium before the reaction begins. The CO_2 peak is produced by decarboxylation of some of the α-ketoglutaric acid in the presence of a base, such as a DNPH. This was established by running the series of experiments shown in Table 2.

By application of the exchange technique to DNPH mixtures derived from cigar (full Havana filler type) smoke

[1] See footnote (1), page 3.

Table 2. Experiments on CO_2 Formation

Sample	Result
α-Ketoglutaric acid only	Negative
DNPH only	Negative
α-Ketoglutaric + DNPH	Peak
α-Ketoglutaric + $Ba(OH)_2$	Peak
Pyruvic acid + $Ba(OH)_2$	Peak
Dry Ice (CO_2) in a syringe	Peak

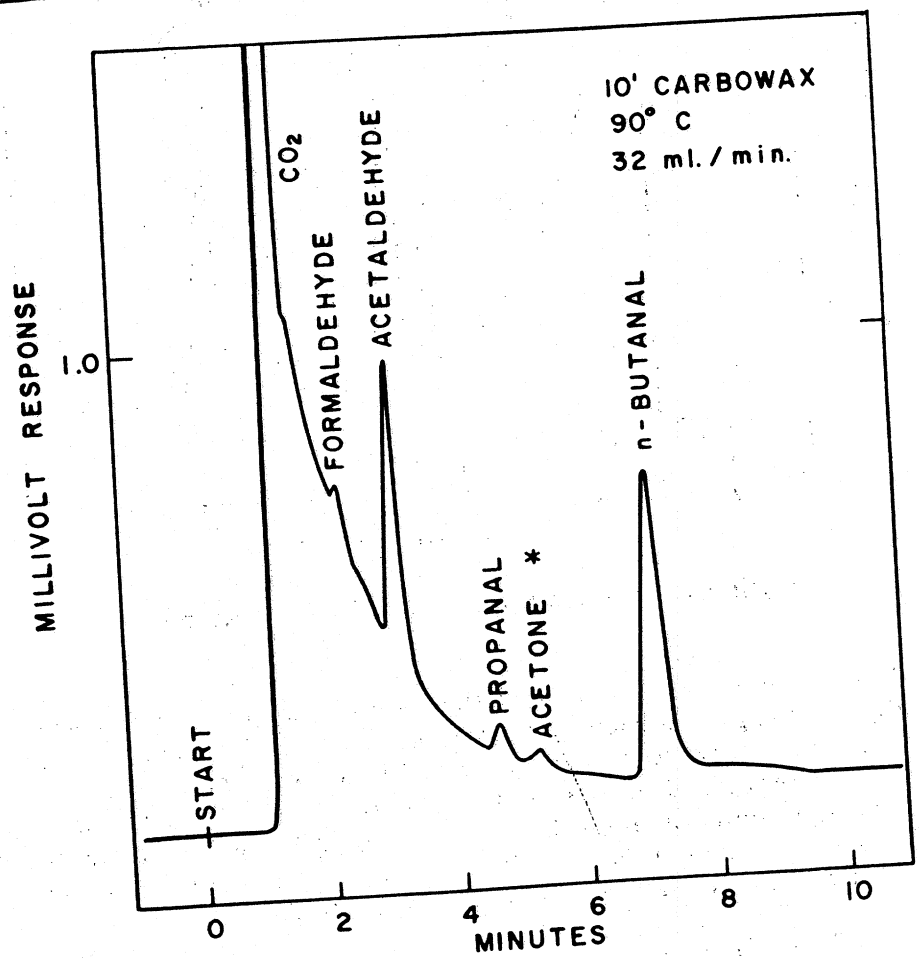

Figure 2. Separation of fraction S-180-AML.
*Iso-butanal or 2,2-dimethyl propanal also possible.

components, it was possible to identify the following carbonyls in one or more of the mixtures examined: formaldehyde, acetaldehyde, propanal, acetone (or possibly iso-butanal or 2, 2-dimethyl propanal), n-butanal and methyl ethyl ketone. Typical examples are shown in Figures 2 and 3.

Acetone could not be separated from iso-butanal or 2, 2-dimethyl propanal in synthetic mixtures. However, since

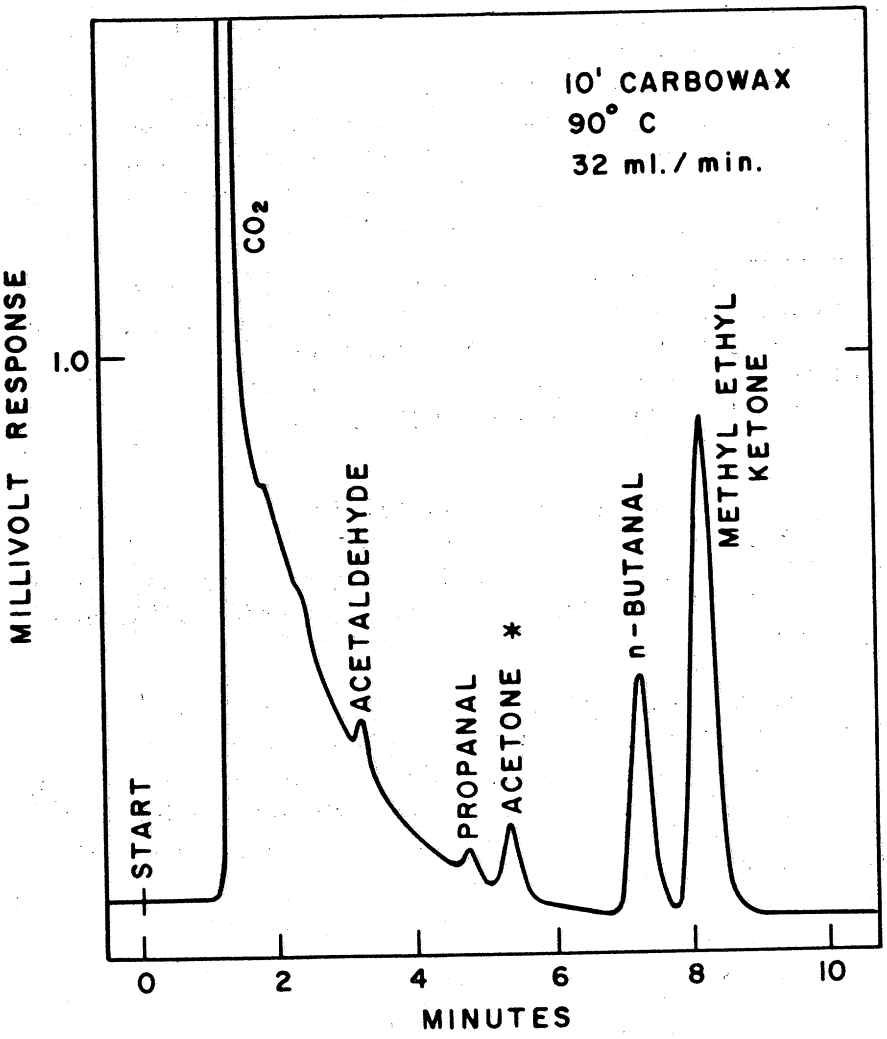

Figure 3. Separation of fraction S-180-A.
*Iso-butanal or 2, 2-dimethyl propanal also possible.

our previous work[2] indicated the presence of acetone in smoke fractions, it is believed that the unknown peak is the ketone. Although we have detected the presence of a few minor components not yet identified, the above compounds appear to be the major carbonyls of the smoke as resolved by this method.

In general, the 10-foot Carbowax column was found to be superior to the 5-foot Polyester column. This was particularly true in working with formaldehyde and acetaldehyde, where proximity to the CO_2 peak was a limiting factor in their detection. Formaldehyde could not be resolved on the Polyester column, while acetaldehyde had to be present in relatively high concentration for detection on this column. Since the smoke components are mainly in the range of C_1-C_4, the Carbowax column was used more extensively in this study.

Although the usual procedure calls for the use of solid samples of DNPH's, it is possible to run the oily type samples often encountered in DNPH reactions. This is done by adding sufficient α-ketoglutaric acid to provide a mixture dry enough to enter the capillary exchange tube.

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[2] Schepartz, A. I., The Chemistry of Cigar Smoke. II. Some Components of the Neutral Fraction. Tobacco Science 4: 12-16 (1960).

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